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Different approaches to assess the environmental performance of a cow manure biogas plant

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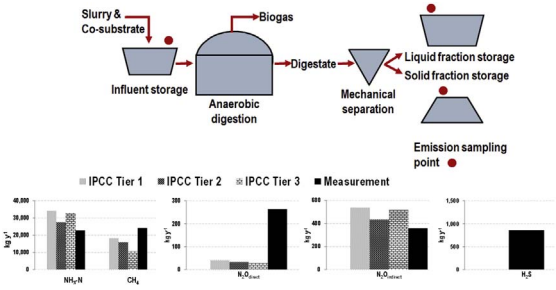
GRAPHICAL ABSTRACT



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ABSTRACT

In intensive livestock production areas, farmers must apply manure management systems to comply with governmental regulations. Biogas plants, as a source of renewable energy, have the potential to reduce environmental impacts comparing with other manure management practices. Nevertheless, manure processing at biogas plants also incurs in non-desired gas emissions that should be considered. At present, available emission calculation methods cover partially emissions produced at a biogas plant, with the subsequent difficulty in the preparation of life cycle inventories. The objective of this study is to characterise gaseous emissions: ammonia (NH_3-N), methane (CH_4), nitrous oxide ($N_2O_{indirect}$, and N_2O_{direct}) and hydrogen sulphide (H_2S) from the anaerobic co-digestion of cow manure by using different approaches for preparing gaseous emission inventories, and to compare the different methodologies used. The chosen scenario for the study is a biogas plant located next to a dairy farm in the North of Catalonia, Spain. Emissions were calculated by two methods: field measurements and estimation, following international guidelines. International Panel on Climate Change (IPCC) guidelines were adapted to estimate emissions for the specific situation according to Tier 1, Tier 2 and Tier 3 approaches. Total air emissions at the biogas plant were calculated from the emissions produced at the three main manure storage facilities on the plant: influent storage, liquid fraction storage, and the solid fraction storage of the digestate. Results showed that most of the emissions were produced in the liquid fraction storage. Comparing measured emissions with estimated emissions, NH_3, CH_4, $N_2O_{indirect}$ and H_2S total emission results were in the same order of magnitude for both methodologies, while, N_2O_{direct} total measured emissions were one order of magnitude higher than the estimates. A Monte Carlo analysis was carried out to examine the uncertainties of emissions determined from experimental data, providing probability distribution functions. Four emission

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inventories were developed with the different methodologies used. Estimation methods proved to be a useful tool to determine emissions when field sampling is not possible. Nevertheless, it was not possible to establish which methodology is more reliable. Therefore, more measurements at different biogas plants should be evaluated to validate the methodologies more precisely.

1. Introduction

Manure management is one of the greatest challenges for farmers. In intensive livestock production areas, an appropriate management of manure is necessary, not only to comply with legislation –for instance, when it comes to groundwater pollution by nitrates from agricultural sources (EEC, 1991; Generalitat de Catalunya, 2009), ammonia emission ceilings (EEC, 2001) or the use of renewable energy targets for reducing greenhouse gases (EEC, 2009)–, but also as a matter of social concern. On the other hand, in the framework of a circular economy, manure should be considered a valuable resource. From this point of view, manure processing technologies could be helpful to close nutrient cycles while reducing emissions to the environment. The implementation of technologies designed to protect the environment is variable across Europe but those methods perceived as good farming practice, or those which benefit the farmer in other ways, are the most widespread (Loyon et al., 2016). The selection of a particular manure processing technology depends, among other things, on technological knowledge, implementation feasibility, local constraints, economic viability, and farm management strategy (Flotats et al., 2011).

In this context, biogas plants are considered as an efficient solution to improve manure management and to mitigate pollution problems while producing renewable energy (Massaro et al., 2015). Nevertheless, manure processing at biogas plants also incurs in non-desired gas emissions. The sustainability of anaerobic digestion plants has been analysed from the perspective of life cycle assessment (Cherubini et al., 2015; Lijó et al., 2014; Poeschl et al., 2012a, b). A LCA requires a detailed inventory for the analysed system, compiling all inputs and outputs in the product life cycle. The assessment of emissions is a key point in the preparation of an inventory and a variety of methods are available to calculate emissions. It is necessary to pay attention to the selection of the method of emission calculation in order to assess the amount of emissions from manure management systems (Braschel and Posch, 2013). On the other hand, emission factors can be determined at laboratory and pilot scale experiments (Perazzolo et al., 2015), and both emission measurements and estimations can be used to gain knowledge about emissions produced at field scale (Owen and Silver, 2015; Vac et al., 2013).

Field emission measurement presents both advantages and drawbacks. Emission sampling provides the amount of gas released for specific climatic conditions and local geographic characteristics (Sommer et al., 2000). However, emission sampling is an expensive and time-consuming technique. Due to physical and structural constraints, it could be difficult to obtain a representative characterisation of all emission points. Therefore, when sampling of emissions is not affordable, an estimation, using normalized methods, can be useful (Storm et al., 2012).

International organisations provide guidebooks to compile an atmospheric emission inventory, (EEA, 2013; IPCC, 2006). Different estimation proxies can be reached depending on data availability and the complexity of the methodology applied. The IPCC guidebook (IPCC, 2006) defines Tier 1, Tier 2, and Tier 3; being Tier 1 the simplest method and Tier 3 the most complex one. These guidebooks provide algorithms and emission factors to estimate, among others, CH_4, NH_3 and N_2O emissions from some of the most usual manure management systems (e.g. storage ponds, composting, etc.), but they are not detailed for other increasingly common practices as by-product storage from a processing plant. After manure treatments, processed manure may change its physical and chemical characteristics. For instance, during anaerobic digestion, easily degradable C is consumed and thus, less organic matter is available to produce "uncontrolled" CH_4, which leads to lower CH_4 emission capacities from the digestate than from untreated slurry (Rodhe et al., 2015). Therefore, it is necessary to develop and adapt methodologies for such specific situations in order to estimate the emissions occurring in these processing plants.

The main objective of the present study was to compare different approaches to characterise gas emissions from a biogas plant processing cow manure and industrial food waste. For this purpose, different methods were used and compared: field sample measurement and emission estimation, following the IPPC adapted guidelines. Additionally, a simplified procedure to estimate air emissions from the storage of anaerobic digestion of manure by-products is provided to prepare a biogas plant emission inventory.

2. Materials and methods

The emissions included in this study were those produced during the storage and processing of manure. The characterisation of emissions was done by field emission measurement and by the calculation of estimates. The emissions selected for the characterisation of the biogas plant were ammonia (NH_3), methane (CH_4) and nitrous oxide (N_2O) gases, due to their relevance in manure management systems and their contribution to environmental impact. Hydrogen sulphide (H_2S) was also considered, due to its contribution to acidification and potential for unpleasant odour generation.

2.1. Processing plant description

The scenario for the case in study was a dairy farm located in the North of Catalonia, Spain, with an average of 920 cattle heads. The farm included two distinct areas: the farm itself, with all the dairy cattle facilities, and a biogas plant. The slurry was stored in the influent storage covered pond (129 m^3). The co-substrate was stored in a covered pond (59 m^3) next to the influent storage pond. The co-substrates used in the plant were mainly organic waste from food industry and sewage sludge from wastewater treatment plants. The addition of co-substrate, which was below 20%, aimed to increase biogas production. The influent was estimated to remain in the influent storage pond (64 m^2) for around two days. Then, the slurry was pumped to the anaerobic digesters (AD), first to two primary AD (AD1′ and AD1″, 2078 m^3 each) and then from the primary to the secondary AD (AD2, 1450 m^3). Digesters consisted of continuous stirred-tank reactors (CSTR). The anaerobic digestion of slurry and co-substrate was conducted at mesophilic conditions (37 °C) with a hydraulic retention time (HRT) of about 50 days. Biogas was conducted to the CHP engine (500 kW) to produce electrical and thermal energy. This electricity was sold to the grid and the thermal energy was used to heat the reactors. The digestate was mechanically separated with a screw press separator, producing a liquid and a solid fraction. The liquid fraction was stored at an un-covered storage pond (2015 m^2; 10,000 m^3) during six months, and the solid fraction was composted in trenches (4 trenches of 3.5 m · 20 m ·1.5 m each) for four months. A gas purification system to eliminate H_2S from the biogas is installed before the CHP engine.

2.2. Sampling procedure

Emission sampling was carried out with a total of eight sampling campaigns. The sampling days were programmed so that the samples

were collected coinciding with the day after the liquid fraction storage pond was filled and the day before the pond was emptied. Therefore, samples were collected every two months approximately. This sampling schedule was carried out to give insight into the specific management of the treatment plant evaluated.

2.2.1. Emission sampling and calculations

Field emission measurements were made at the influent storage tank (IS) and at the digestate liquid and solid fraction final storages, namely the liquid fraction storage compartment (LFS) and the solid fraction storage compartment (SFS) corresponding to the compost piles.

All samplings were conducted in the morning, between 10:00 and 14:00. Climate conditions in the area were collected from the nearest weather station in Banyoles (Meteocat, 2016). Detailed information on temperature, humidity, rainfall and wind for each sampling day is presented in Table S1 (supplementary material). Air samples were collected with a floating wind tunnel set up following the Lindvall Hood Method (EPA, 2001). The Lindvall Hood and other similar dynamic chambers are used not only for odour measurements but also for other emissions sampling (Misselbrook et al., 1998; Rostami et al., 2015; van Belois and Anzion, 1992). It should be mentioned that the Lindvall Hood method could overestimate emissions as the method modify the local conditions that affect the release of gases. The hood surface area was 0.92 m^2. In every sampling campaign the tunnel was placed in the same point. When placed over the liquid surface, the chamber sank few centimetres into the pond forming a seal between the surface and the air within the wind tunnel, avoiding gas losses. In the case of the compost piles, the chamber should penetrate also several centimetres into the compost in order to seal it. A ventilator was connected to the inlet opening of the hood to drive a constant air flow inside the hood. The airflow velocity in the wind tunnel was set following EPA recommendations for the Lindvall Hood (EPA, 2001), which must be between 0.2 and 0.3 m s^{-1}. Before emission measurements, airflow velocity was measured with an anemometer and airflow velocity was adjusted accordingly. When calculating emissions, the value of the background concentration in the atmosphere was subtracted. For each of the analysed compounds the sampling procedure was different and is detailed hereunder.

Ammonia nitrogen (*NH_3-N*) *emissions* were trapped bubbling a known volume of air into two serial glass midget impringers containing 10 mL of sulphuric acid 0.1 N. Three replicates per point were taken for 5 min sampling time periods, each one of them at a flow rate of 1 L min^{-1}, approximately.

Hydrogen sulphide (*H_2S*) *emissions* were sampled using a prefilter of 0.45 μm of pore size (Zefluor Polytetrafluoroethylene), supported by a porous plastic support pad, 25 mm of diameter, followed by a 10 cm glass tube containing 400/200 mg of coconut shell charcoal, for a 20 min sampling time period, at a flow rate of 0.2 L min^{-1}. Two replicates per point were collected in this case.

Methane (*CH_4*) *and direct dinitrogen oxide* (*N_2O_{direct}*) *emissions* were carried out using an air sampling pump, connected to a 3 L air sample bag (SamplePro FlexFilm) at a flow rate of 1 L min^{-1}. Just one replicate per point was taken but samples were analysed per duplicate.

To calculate the specific emission rates, firstly it is necessary to know the "hood constant", which can be calculated as:

$$L = F_{path} / A \quad (1)$$

where L is the hood constant, F_{path} is the flow path cross section area (m^2) and A is the covered area (m^2). In this case the hood constant was 0.0085, F_{path} was 0.0079 m^2 and A was 0.9216 m^2.

Once the hood constant was known, the specific emission rates (E_{sp}, mg m^{-2} s^{-1}) could be calculated from the concentration measured at the exit of the hood (C_{hood}, mg m^{-3}) and the flow velocity (V, m s^{-1}), as follows with equation (2):

$$E_{sp} = C_{hood} \cdot L \cdot V \quad (2)$$

Indirect dinitrogen oxide (*$N_2O_{indirect}$*) *emissions* result from volatile nitrogen losses that occur primarily in the forms of ammonia and NO_x (IPCC, 2006). Indirect N_2O emissions could not be measured and they were calculated with equation (5), see section 2.4.

2.2.2. Manure sampling and mass balance

In order to characterise the performance of the biogas plant, liquid and solid manure samples were collected on a monthly basis and characterized, carrying out a mass and component balance of the entire plant. Samples were taken from the influent storage tank after 60 min of intense mixing, the effluent from AD2, the liquid and solid fractions of digestate after solid-liquid separation, LFS, and SFS. In the three storage ponds where emission measurements took place, manure samples were collected next to where the Lindvall Hood was placed. Solid samples were collected from different points of the compost pile at 20–30 cm depth. One replicate per point was randomly taken.

The yearly component mass balance for each of the solid and liquid streams (total solids, volatile solids, etc.) were calculated taking into account: the influent mass flow of the treatment plant (data provided by the biogas plant operators); the removal efficiency in the anaerobic digestion (AD was considered to remove 10% of the mass due to TS degradation and the subsequent CH_4 production); the separator efficiency measured in the plant; and the average composition of each stream.

2.3. Analytical methods

To determine the amount of ammonium nitrogen (NH_3-N) emissions, samples were analysed using a modified method based on Conditional Test EPA Method (CTM-027) sampling (EPA draft, 1997), and colorimetric NIOSH Method 6015 analysis (NIOSH, 1994b). H_2S emissions samples were desorbed from solid sorbent tubes with eluent, and the resulting sulphate analysed by ionic chromatography following the NIOSH 6013 Method instructions (NIOSH, 1994a). The amount of CH_4 was determined using a THERMO TRACE 2000 (Thermo Fisher Scientific, USA) gas chromatograph equipped with a flame ionization detector (FID). N_2O emissions were determined with an Agilent 7820A (Agilent, USA) GC system using an electron capture detector (ECD).

Standard methods were used to analyse total Kjeldahl nitrogen (TKN) (4500-Norg C), ammonium nitrogen (NH_4^+-N) (4500-NH3 B C), pH (4500- H + B), total solids (TS) (2540 B) and volatile solids (VS) (2540 E), (APHA, 2014), and the chemical oxygen demand (COD) following de method described in Noguerol-Arias et al. (2012). Potassium (K) was analysed by ionic chromatography following Standard Method 4110 B. Total phosphorus (P) was analysed by colorimetric Standard Method 4500-P C.

Anaerobic biodegradability test: In order to determine the methane producing capacity (B_0) of manure, anaerobic biodegradability tests of the digestate as well as the liquid and solid fractions of the digestate were performed –after mechanical separation–following the methodology described in Silvestre et al. (2011).

2.4. Estimation of emissions – IPCC method

The International Panel on Climate Change (IPCC) guidelines (IPCC, 2006) were used as guidance to estimate CH_4, N_2O and NH_3-N emissions, even if equations were adapted to the present case in study.

The equations and emission factors to calculate emissions were the following:

Methane (CH_4) emissions (EF_{CH4}, kg CH_4 y^{-1}) were estimated with equation (3)

$$EF_{CH4} = VS \cdot B_0 \cdot 0.67 \cdot MCF / 100 \quad (3)$$

where, EF_{CH4} is the CH_4 emission factor (kg CH_4 y^{-1}), *VS* (kg VS y^{-1}) stands for volatile solids excreted or contained in the manure, B_0 (m^3

CH_4 kg VS^{-1}) is the maximum VS methane production capacity, *0.67* is the conversion factor of m^{-3} CH_4 to kg CH_4, and *MCF* (%) is the methane conversion factor for each manure management system according to the climate region.

According to IPCC definitions of manure management systems, slurry storage previous to anaerobic digestion corresponds to the system *Liquid/Slurry*. However, the digestate storage compartment could not be appropriately defined as *Liquid/Slurry* because after anaerobic digestion the characteristics of manure change significantly and may produce methane at a different rate. Therefore, specific B_0 values, as a result of the anaerobic biodegradability tests, were established to estimate methane emissions from fresh slurry and digestate storages.

Nitrous oxide (*N_2O*) *direct emissions* (N_2O_{direct}, kg N_2O y^{-1}) were calculated following equation (4).

$$N_2O_{direct} = N_{ex(T)} \cdot EF \cdot 44 / 28 \quad (4)$$

where $N_{ex(T)}$ (kg N y^{-1}) is the total amount of N excreted or contained in the manure, *EF* (kg N_2O-N kg N^{-1}) is the emission factor for the type of manure management system, and *44/28* is the N_2O-N emissions to N_2O emissions conversion factor.

Nitrous oxide (N_2O) indirect emissions (kg N_2O y^{-1}) were estimated using Equation (5).

$$N_2O_{indirect} = N_{volatilization} \cdot EF \cdot 44 / 28 \quad (5)$$

where $N_{volatilization}$ (kg NH_3-N + NO_x-N volatilised) is the total amount of volatilised N, *EF* is the emission factor for indirect N_2O emissions (default value is 0.01 kg N_2O-N (kg NH_3-N + NO_x-N volatilised)$^{-1}$ according to IPCC, Table 1), and *44/28* is the N_2O-N emissions to N_2O emissions conversion factor.

Ammonia (NH_3) emissions (kg NH_3-N + NO_x-N volatilised) were calculated with equation (6):

$$N_{volatilization} = N_{ex} \cdot Frac / 100 \quad (6)$$

where N_{ex} (kg N y^{-1}) is the total amount of N excreted or contained in the manure and *Frac* (%) is the fraction of nitrogen that volatilises.

Depending on the specific livestock information and the complexity of the analysis, three approaches can be followed to estimate emissions from manure management, namely Tier 1, Tier 2, and Tier 3.

2.4.1. Tier 1 approach

In this approach, the characterisation of manure was done using IPCC default data: Nitrogen excreted per dairy cattle in Western Europe (100 kg N $head^{-1}$ $year^{-1}$) and volatile solid content in manure (5.1 kg VS $head^{-1}$ day^{-1}) (IPCC, 2006). The model was adapted to calculate CH_4 emissions considering a 100% slurry storage management system and, for that system, selecting MCFs according to the average annual temperature.

To calculate emissions of by-product storage, emission factors from literature and several other considerations were taken into account: 1- Different manure storage time periods before and after anaerobic digestion; 2- Total nitrogen content in manure was the same before and after anaerobic digestion (Rodhe et al., 2015). Nitrogen emissions at the influent storage pond and at the final storage pond were related to the manure residence time period in the pond; 3-Total nitrogen and volatile solids content in the solid fraction after screw press separation were 6% and 23%, respectively (Møller et al., 2002); 4- Ammonia losses in the liquid fraction of the digestate were considered to be of 40%, just like in the raw manure storage compartment, and losses in the solid fraction to be of 30% (IPCC, 2006); 5- Volatile solids reduction in anaerobic digestion was estimated at 45% (El-Mashad and Zhang, 2010); 6- The maximum methane producing capacity for the digestate was 121 m^3 CH_4 kg VS^{-1} (Rodhe et al., 2015).

2.4.2. Tier 2 approach

In this case, the characterisation of excreted manure was done using regional data from Catalonia. Nitrogen excreted per dairy cattle was estimated at 80.22 kg N $head^{-1}$ $year^{-1}$ (Generalitat de Catalunya,

Table 1
Emission factors (EF) used to estimate NH3-N, CH4 and indirect N2O emissions in biogas plant compartments: influent storage (IS), liquid fraction storage (LFS) and solid fraction storage (SFS). Data sources are presented for Tier 1, Tier 2 and Tier 3 approaches.

Emission	Storage	Factor	Tier 1	Tier 2	Tier 3
NH_3-N	IS	N, available (kg N y^{-1})	86,613[a]	69,880[b]	152,642[c]
		Storage time (yearly %)	1.3	1.3	1.3
		EF (% NH_3-N + NO_x-N loss)	40[a]	40[a]	40[a]
	LFS	N, available (kg y^{-1})	81,407[a+e]	65,681[b+e]	73,779[c]
		N separator efficiency (%)	94.0[e]	94.0[e]	–
		Storage time (yearly %)	98.7	98.7	–
		EF (% NH_3-N + NO_x-N loss)	40[a]	40[a]	40[a]
	SFS	N, available (kg y^{-1})	5,205[a+e]	4,200[a+e]	3,557[c]
		N separator efficiency (%)	6.0[e]	6.0[e]	–
		EF (% NH_3-N + NO_x-N loss)	30[a]	30[a]	–
CH_4	IS	VS, available (kg VS y^{-1})	1,717,234[a+d]	1,498,371[b+d]	2,910,802[c]
		Storage time (yearly %)	1.3[d]	1.3[d]	–
		MFC CH_4 (%)	27; 29[a]	27; 29[a]	27; 29[a]
		B_0 (m^3 CH_4·kg VS^{-1})	0.24[a]	0.24[a]	0.273[f]
	LFS	VS, available (kg VS y^{-1})	727,437[a+e+g]	634,725[b+e+g]	519,989[c]
		VS post AD (%)	55[g]	55[g]	–
		VS separator efficiency (%)	77.0[e]	77.0[e]	–
		MFC CH_4 (%)	27; 29[a]	27; 29[a]	27; 29[a]
		B_0 (m^3 CH_4·kg VS^{-1})	0.121[h]	0.121[h]	0.086[f]
	SFS	VS, available (kg VS y^{-1})	217,041[a+e+g]	189,379[b+e+g]	103,832[c]
		VS post AD (%)	55[g]	55[g]	–
		VS separator efficiency (%)	23.0[e]	23.0[e]	–
		MFC CH_4 (%)	4.0[a]	4.0[a]	4.0[a]
		B_0 (m^3 CH_4·kg VS^{-1})	0.121[h]	0.121[h]	0.100[f]
$N_2O_{indirect}$	IS, LFS, SFS	N_2O EF (kg N_2O-N (kg NH_3-N + NO_x-Nvol)$^{-1}$)	0.01[a]	0.01[a]	0.01[a]
N_2O_{direct}	SFS	N, available at SFS (kg y^{-1})	5,205[a+e]	4,200[b+e]	3, 557[c]
		N separator efficiency (%)	6.01[e]	6.01[e]	–
		Direct N_2O EF (kg N_2O-N kg N $total^{-1}$)	0.005[a]	0.005[a]	0.005[a]

[a]IPCC, 2006; [b]Regional data, Generalitat de Catalunya, 2009; [c]Analytical data; [d]Assumption; [e]Møller et al., 2002; [f]Laboratory test; [g]El-Mashad and Zhang, 2010; [h]Rodhe et al., 2015.

2009) and the volatile solid content in manure was 4.45 kg VS head^{-1} day^{-1}. To calculate CH_4, NH_3 and N_2O emissions, the same considerations used in Tier 1 were taken into account.

2.4.3. Tier 3 approach

The characterisation of manure was done using analytical data. The total excreted nitrogen resulted in 148,109 kg N y^{-1} and total VS in 2,318,869 kg VS y^{-1}. Maximum methane producing capacities were obtained from the biodegradability test (B_0, in m^3 CH_4 kg VS^{-1}). The NH_3 and N_2O emission factors used were the same as those used in the Tier 1 and Tier 2 approaches.

A summary of all considered factors and hypothesis used to estimate emissions is presented in Table 1.

2.5. Uncertainty analysis

An uncertainty analysis was carried out for manure composition parameters and emissions obtained from analytical data. Standard deviation was included in results for mass and component balance of manure samples, emission rates, emission field measurements and emission Tier 3 estimates, as these were the results obtained from experimental data.

Measured and Tier 3 estimated emissions were analysed with an additional statistical test in order to assess the uncertainty of the emissions. A Monte Carlo analysis was conducted as less than 30 measurement and estimation values were available in the present study (Maurice et al., 2000). Monte Carlo simulation gives the probability distributions of output data. In this analysis, a random emission value from an emission range is selected for a distribution model in each run or iteration. Monte Carlo simulation calculates the model a programmed number of times, each time using different randomly-selected values. Emissions are independent random variables and therefore lognormal distribution was used for the emission model, as emission parameters were non-negative values and standard deviation was greater than 30% (Ramírez et al., 2008). The lognormal distribution is the probability distribution where the natural logarithm of the observed values are normally distributed (Weidema et al., 2013). The software tool SimaPro version 8.3.0 was used to carry out the Monte Carlo simulation. In this analysis, the entire simulation was run 10,000 times for each gas emission and for the emission comparisons (Meyer, 2007; Sonnemann et al., 2003). The confidence interval was 95%. The comparison of measurements and estimates for a certain gas was done running the simulation of both total emissions at the same time. In this case, the probability distribution function was for the difference between measured and estimated values.

Table 3
Gas emission rates (mean and standard deviation, mg m^{-2} s^{-1}) of field measurements per point of storage: influent storage (IS), liquid fraction storage (LFS) and solid fraction storage (SFS).

Storage	NH_3-N mg m^{-2} s^{-1}	CH_4 mg m^{-2} s^{-1}	N_2O-N mg m^{-2} s^{-1}	H_2S mg m^{-2} s^{-1}
IS	0.032 ± 0.021	0.983 ± 0.887	0.002 ± 0.001	0.027 ± 0.014
LFS	0.356 ± 0.172	0.235 ± 0.233	0.002 ± 0.001	0.019 ± 0.013
SFS	0.152 ± 0.164	0.136 ± 0.096	0.003 ± 0.001	0.020 ± 0.021

3. Results

Results obtained from manure sampling, field emission measurements, and from Tier estimations were useful to characterise the emissions produced at the biogas plant. Calculated estimates from the different IPCC approaches were assessed and their respective results compared. Finally, results obtained from field measurements were compared with the estimates. Results are presented in Tables 2 and 3, and in Figs. 1 and 2.

3.1. Biogas plant characterisation

Results for the characterisation of the biogas plant were from the analysis of sampled materials and emission measurements at the biogas plant, and they are detailed in the following sections.

3.1.1. Biogas plant performance

As can be seen in Table 2, between the influent and the effluent of the anaerobic digesters (AD2 sample, namely digestate) there is a mass flow reduction of TS, VS and COD, as a result of organic matter degradation and biogas production. The slight decrease in TKN between these two samples can be attributed to the NH_3 released together with the biogas. Oppositely, ammonia nitrogen showed a 21% increase, due to organic nitrogen ammonification.

Mechanical separation produced two fractions with different nutrient contents. The liquid fraction contained 95.4% of TKN and 77.6% of VS in the original non-separated digestate. Similarly, 95.6% of the

Table 2
Mass and component balance of manure samples at the biogas plant. Annual average values and standard deviation. IS: influent storage; AD1′ and AD1″: Primary anaerobic digestors; AD2: Secondary anaerobic digestor: LF: liquid fraction; SF: Solid fraction; LFS: liquid fraction storage; SFS: solid fraction storage; EC: Electrical conductivity; TS: Total solids; VS: Volatile solids; COD: Chemical oxygen demand; TKN: Total Kjehldahl nitrogen; NH_4-N: Ammonium nitrogen; P: Phosphorus; K: Potassium.

Component	IS	AD1′	AD1″	AD2	LF	SF	LFS	SFS
Flow (t y^{-1})	38,325 ± 1864	17,337 ± 63	17,340 ± 3	34,683 ± 137	33,888 ± 235	989 ± 245	33,888 ± 235	396 ± 98
pH	6.4 ± 0.6	8.0 ± 0.2	7.9 ± 0.2	8.0 ± 0.2	8.1 ± 0.2	8.5 ± 0.5	8.1 ± 0.3	8.0 ± 0.6
EC (mS)	7.8 ± 4.3	– –	– –	– –	10.8 ± 5.3	2.8 ± 3.1	8.7 ± 4.5	2.9 ± 3.5
TS (t y^{-1})	3382 ± 779	780 ± 150	784 ± 160	1570 ± 372	1225 ± 243	279 ± 73	798 ± 454	125 ± 46
VS (t y^{-1})	2911 ± 595	553 ± 113	554 ± 122	1100 ± 284	821 ± 174	237 ± 61	520 ± 329	104 ± 37
COD (t y^{-1})	5911 ± 1702	965 ± 200	948 ± 184	1829 ± 357	– –	– –	– –	– –
TKN (t y^{-1})	153 ± 30	69 ± 7.6	69 ± 8.0	140 ± 19	129 ± 13	6.3 ± 1.8	73.8 ± 18.0	3.6 ± 1.7
NH_4-N (t y^{-1})	73.8 ± 10	43.9 ± 6.2	43.1 ± 3.9	89.2 ± 8.4	84.0 ± 9.3	3.9 ± 2.0	53.0 ± 11	0.7 ± 0.4
P (t y^{-1})	27.3 ± 6.5	– –	– –	– –	21.0 –	2.2 ± 0.9	12.9 ± 8.0	1.0 ± 0.4
K (t y^{-1})	42.7 ± 15.7	– –	– –	– –	40.7 ± 12.1	0.7 ± 0.5	34.2 ± 15.7	0.3 ± 0.2

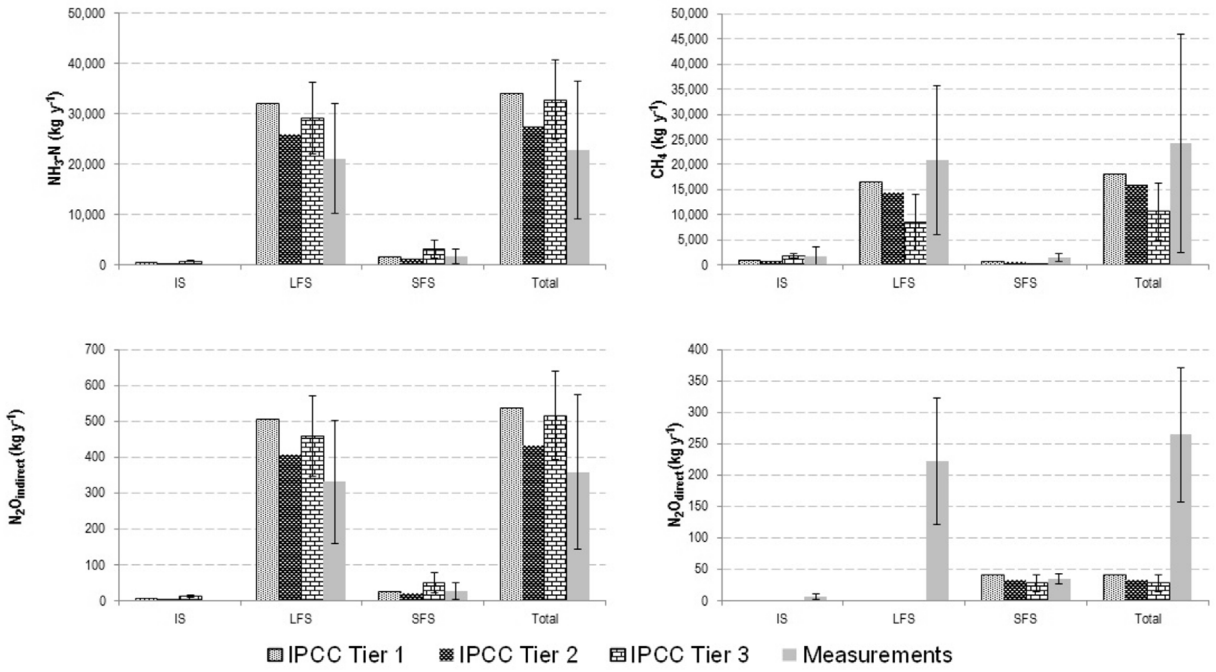

Fig. 1. NH_3-N, CH_4, $N_2O_{indirect}$ and N_2O_{direct} emission values for IPCC models and field measurements at the influent storage (IS), the liquid fraction storage (LFS) and the solid fraction storage (SFS), mean value and standard deviation for Tier 3 and field measurement comparison.

NH_4-N in the original digestate remained in the liquid fraction, the same separation efficiency as for TKN. The solid fraction was rich in organic matter (238.9 g L^{-1} VS) and phosphorus (2.28 g L^{-1} P) and the liquid fraction was rich in soluble nitrogen (2.45 g L^{-1} NH_4-N) and potassium (1.20 g L^{-1} K). The TAN/TKN ratio was similar in both the liquid and solid fractions of the digestate, 0.65 and 0.62 respectively, but in the final storage pond it increased up to 0.72, probably due to an ammonification process occurred during the long period of storage. Contrarily, the TAN/TKN ratio was much lower in the final compost (0.20) – biomass growth during the composting process fixing ammonia, high temperatures reached during the process favouring ammonia emissions, and the nitrification process, explain these differences

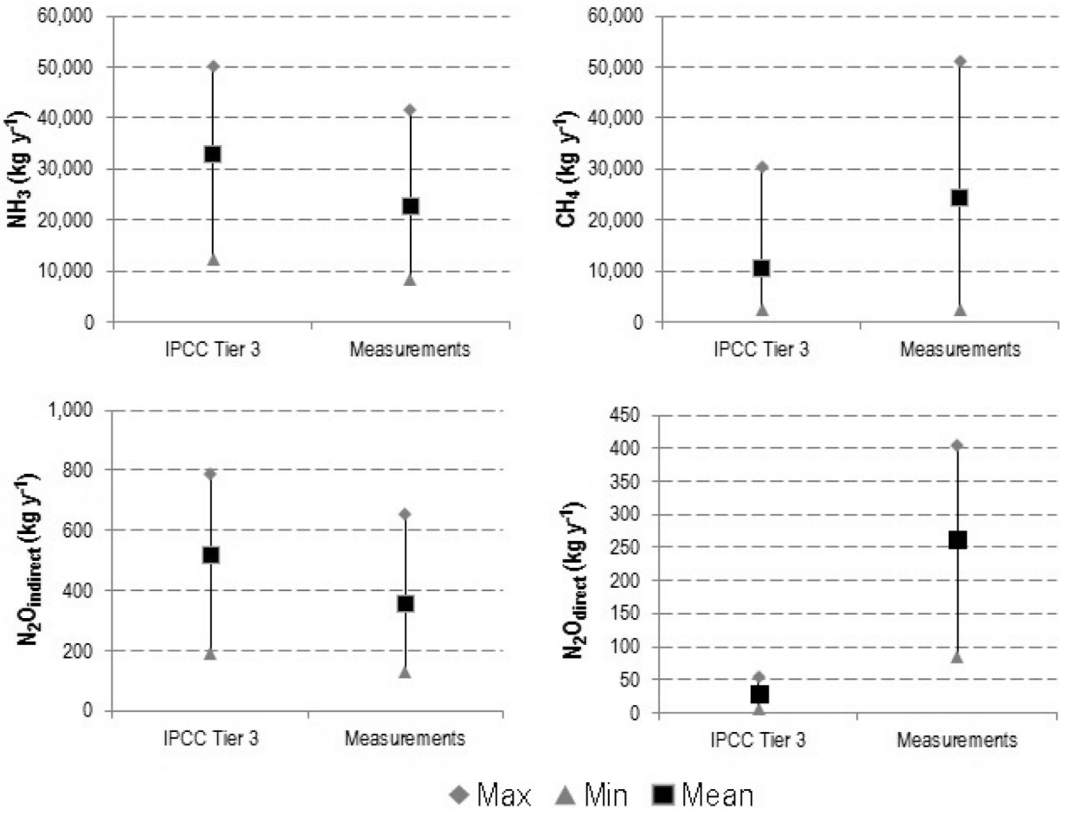

Fig. 2. Tier 3 estimates and field measurements, mean value with the maximum-minimum value range.

in the ratio. These processes were confirmed by the lower amount of NH_4-N in the final storage pond and compost piles, with respect to the liquid and the solid fraction, respectively. During the liquid fraction storage, apart from the aforementioned ammonification process, a basic pH of 8 favoured volatilization of NH_3. From these results, total nitrogen losses amounted to 75.3 t y^{-1}, most of them attributable to ammonia emissions. Nevertheless, sedimentation of solids and the non-representativeness of the samples are issues that should be taken into account when estimating emissions with the mass balance method.

3.1.2. Emission measurement

Emission rates per each type of gas and for each type of storage compartment are presented in Table 3. Per type of storage compartment, the highest emission factors (mg m^{-2} s^{-1}) were for CH_4 in IS and for NH_3-N in LFS and SFS. The CH_4 emission factor in IS was 4.2-fold higher than in the LFS, as CH_4 production is much higher before anaerobic digestion. Even though the capacity to produce CH_4 was reduced after anaerobic digestion, the highest amount of CH_4 emissions per year was produced in LFS. These results can be explained by the fact that storage dimensions and storage time were higher for the liquid fraction (98.7% of the total storage time) than for the influent (1.3% of the total storage time). Consequently, the loss of methane per VS content was higher in LFS (15.3%) than in IS (0.36%). NH_3-N showed the highest emission factor in LFS (0.356 mg m^{-2} s^{-1}) and, taking into account the loss of NH_3-N per nitrogen content, it rose up to 28.6% per TKN content, and to 39.9% per TAN content. The highest N_2O-N emission factor was in SFS (0.003 mg m^{-2} s^{-1}) also taking into account the amount of N_2O produced per TKN content (0.98%). The composting process in aerobic conditions favoured the production of N_2O, whilst the production of N_2O per TKN content was negligible in IS and LFS (0.00% and 0.26%, respectively). For H_2S, the highest emission factor was found in IS (0.027 mg m^{-2} s^{-1}) showing similar values in LFS and in SFS (0.019 and 0.020 mg m^{-2} s^{-1}, respectively).

The highest emissions for all the measured gases were produced in the storage compartment of the liquid fraction of the digestate at the final storage pond (Fig. 1). An emission contribution in a compartment was the ratio between the amount of this emission divided by the total amount of this gas in the biogas plant, in percentage (%). Liquid fraction contributions to the total plant measured emissions were 92.5% for NH_3-N, 86.4% for CH_4, 92.5% for $N_2O_{indirect}$, 84.1% for N_2O_{direct}, and 72.6% for H_2S emissions. These high emission values found at the final storage pond were due to the fact that, after mechanical separation of the digestate, the majority of N and VS content remained in the liquid fraction, and also because the emitting surface of final storage pond was 34-fold larger than influent storage pond emitting surface. Emissions at IS were 0.2% of NH_3-N and $N_2O_{indirect}$, 7.5% of CH_4, 2.6% of N_2O_{direct}, and 7.3% of H_2S; and emissions at SFS were 7.2% of NH_3-N and $N_2O_{indirect}$, 6.1% of CH_4, 13.3% of N_2O_{direct}, and 20.1% of H_2S (Table S2 in supplementary information).

3.2. Emission estimates adapting the IPCC guidelines

For all gases, the highest total estimates were those calculated with the Tier 1 approach, followed by Tier 3 and Tier 2 for NH_3-N and $N_2O_{indirect}$ emissions, and by Tier 2 and Tier 3 for N_2O_{direct} and CH_4 emissions. NH_3-N and $N_2O_{indirect}$ Tier 1 results were 4% and 24% higher than Tier 3 and Tier 2 results, respectively. N_2O_{direct} emissions were 24% higher than Tier 2 and 46% higher than Tier 3 estimates. Methane emissions in Tier 1 were 15% and 71% higher than Tier 2 and Tier 3 emissions, respectively (Table S2).

For each gas and type of storage compartment, Tier 1 emissions were higher than Tier 2 emissions. The emission contribution of the different sampling points was the same in both Tiers and for all gases. This was because the considered emission factors were always the same, the only difference between Tier 1 and Tier 2 being the initial amount of N and VS to calculate emissions.

From IPCC estimations, the results for each different gas emission showed that the storage compartment of the liquid fraction of the digestate produced the highest amount of emissions in the plant, results similar to those obtained by field measurements.

3.3. Methods assessment

In this section, the results from the different field measurements were compared with the estimates. This comparison showed that total emissions at the biogas plant were all in the same order of magnitude for NH_3-N, $N_2O_{indirect}$ and CH_4 gases (Fig. 1). Differences were found when comparing field measurements with estimated total values, being NH_3-N and $N_2O_{indirect}$ measurements lower than any of the estimates and CH_4 measurements higher than any of the estimates. NH_3-N and $N_2O_{indirect}$ field measured emissions were 33%, 17% and 30% lower than Tier 1, Tier 2 and Tier 3 estimates, respectively. In IPCC approach, the amount of NH_3 and N_2O emissions was estimated according to the N content in excreta. The higher N content in Tier 1 and Tier 3 than in Tier 2 delivered higher N emissions in Tier 1 and Tier 3, and consequently, higher differences of N emissions comparing with measurements. Total CH_4 field measured emissions were 33%, 52% and 2.27-fold higher than Tier 1, Tier 2 and Tier 3 estimates, respectively (Table S3).

Other differences could be observed when comparing emissions per type of storage compartment. NH_3-N and $N_2O_{indirect}$ measurements were 53% lower than Tier 3 estimates, and 6% and 31% higher than Tier 1 and Tier 2 estimates, in the SFS. Still, field measurements in the IS were between 86% and 94% lower than the estimates. In this case, even though these differences were so high, they did not exert much impact because the contribution of IS emissions to the total emissions was very small (Table S2).

On the other hand, ratios between measurement and Tier 1, Tier 2 and Tier 3 results were nearly the same at LFS (0.66, 0.81 and 0.72) and total values (0.67, 0.83 and 0.70). This can be explained because the contribution of LFS to total emissions was very high and with similar percentages in Tier estimates and field measurements, being 94.1% in Tier 1 and Tier 2, 88.9% in Tier 3, and 92.5% in field measurements.

In the case of CH_4 emissions, measurements at LFS were 1.27-fold, 1.45-fold and 2.47-fold higher than Tier 1, Tier 2 and Tier 3 estimates, respectively, similar values than when comparing total values (1.33-fold, 1.52-fold and 2.27-fold, respectively) (Table S3). Measured emissions were 5.31-fold higher than Tier 3 in SFS and 5% lower at IS. High contribution of LFS to total emissions was the reason behind these results, 86.4% in field measurements and 79.5% in Tier 3 estimates. On the other hand, Tier 3 estimates showed the lowest results. B_0 used to estimate Tier 3 emissions was obtained from laboratory experiments, the lower methane production capacity of the digestate fractions resulting in these low values.

The highest differences between field measurements and estimates were found in N_2O_{direct} total emission results. Total N_2O_{direct} field-measured emissions were one order of magnitude higher than total emission estimates in all Tiers. In this case, the most significant differences were found in LFS, as N_2O_{direct} emissions of SFS were in the same order of magnitude for all Tiers and field measurements. Field-measured results were 6% and 25% higher than Tier 2 and Tier 3 estimates, respectively, and 14% lower than Tier 1 estimates.

A thorough analysis could be carried out with results from Tier 3 estimates and field measurements as they were figured out from the compilation of multiple field data (n = 24). Therefore, in order to examine the differences between measurements and estimates, the maximum and minimum emission values were considered. Fig. 2 shows the average, maximum and minimum emissions values for all gas emissions. Tier 3 and field measurement emission value ranges were similar for each gas, except for CH_4 maximum and N_2O emissions. NH_3-N, $N_2O_{indirect}$, N_2O_{direct} and CH_4 maximum values were between 1.5-fold and 2.9-fold higher than the mean, and the minimum values were

between 2.7-fold and 10-fold lower than the mean. There were no substantial differences between NH_3-N and $N_2O_{indirect}$ means, maximum and minimum values, but N_2O_{direct} emission value ranges did not match in either average, maximum or minimum values. Total N_2O_{direct} field measurements emissions included emissions from IS, LFS and SFS, whilst estimated Tier 3 N_2O_{direct} emissions only accounted for SFS emissions. CH_4 means and maximums differed considerably, but the minimum value was nearly the same.

3.4. Uncertainty assessment

Monte Carlo simulations provided a probability distribution function of measured and Tier 3 estimated emissions, and the significance of the differences in the comparison of gas measurements with Tier 3 estimates. The results of the Monte Carlo analysis are presented in Table 4, showing the statistical parameters related to the distribution functions of NH_3-N, CH_4, N_2O and H_2S emissions and their comparisons. Results were also represented in histogram graphs showing the obtained probability distributions and are included in the supplementary information (Figs. S1–S9). The shapes of the probability distributions were different for each one of the emissions. NH_3-N, CH_4 and $N_2O_{indirect}$ Tier 3 estimates and N_2O_{direct} measurements showed a more normal distribution than NH_3-N, CH_4 $N_2O_{indirect}$ and H_2S measurements and N_2O_{direct} Tier 3 estimates.

The coefficient of variation (CV) is the ratio between the standard deviation and the mean, and indicates the dispersion of the measures around the mean. NH_3-N, N_2O and estimated CH_4 CVs were between 8.1% and 35.3%. CH_4 and H_2S CVs of measurement were higher than 200%, showing the highest uncertainties.

In the comparison of measurements with Tier 3 estimates, the probability distribution function was for the difference between measurements and estimates. Results showed that the probability of the runs with NH_3-N measurement values higher or equal than estimate values was 12.2%, similar to the 13.7% probability of $N_2O_{indirect}$. The probability of measurement values higher or equal than estimate values was 37.8% for CH_4 and 100% N_2O_{direc} emissions. In this comparative analysis, CH_4 differences also showed the highest CV.

4. Discussion

Emissions producing relevant environmental impact from a biogas plant were selected. Field measurements and the modified IPCC estimation approaches used in the study served to characterise gas emissions. To calculate emissions of anaerobic digestion by-products, different hypothesis based on literature and laboratory results were established. These methods can be useful for preparing an emission inventory. Nevertheless, each method shows advantages and drawbacks that should be taken into account in their application. Results to characterise the biogas plant and the methods used are discussed in this section.

Based on the four emission inventories the biogas plant under study could be assessed. Even emission values showed high differences among the different approaches used, total emissions were all in the same order of magnitude for NH_3-N, $N_2O_{indirect}$ and CH_4 gases. The storage of liquid fraction of digestate made the highest emissions in the plant. Therefore, actions should focus in digestate phase in order to reduce emissions and environmental impacts. Anaerobic digestion can be used in combination with other processing technologies. Some of them are more effective when performed after anaerobic digestion, such as evaporation (Bonmatí et al., 2003; Bonmatí and Flotats, 2003b) or ammonia removal by air stripping (Bonmatí and Flotats, 2003a). Moreover, anaerobic digestion can be integrated with struvite precipitation in order to remove ammonia and phosphates from manure, producing a valuable fertilizer in the meantime (Cerrillo et al., 2015), and also combined with a composting process of the solid fraction of the digestate (Bustamante et al., 2013, 2014). Biogas production is also a clean energy source when processing other organic wastes such as the organic fraction of municipal solid waste or sewage sludge from wastewater treatment plants (Silvestre et al., 2011).

Regarding field emission measurements sampling representativeness is a critical point, due to the high number of samples needed to cover the high variability in conditions. In the present case, the two-year period could be long, but with the eight sampling campaigns carried out the representativeness of the samples could not be assured for all the different climates and plant operation conditions throughout an entire year. On the other hand, emission sampling is time-consuming, requires technical knowledge, is not always affordable, and could over- or under-estimate emissions; e.g. Lindvall Hood method is said to overestimate emissions because local conditions are modified during sampling. This is where emission models come as an interesting tool to determine emission rates when field measurements are not possible. Nevertheless, it would be advisable to test the different models in local conditions, and to compare them with field measurements in order to establish their accuracy. In order to validate these methodologies, more biogas plants should be analysed.

The IPCC guidelines provided different approaches to determine CH_4, NH_3 and N_2O emissions based on the amount of VS produced by cows, in the case of CH_4 emissions, and on the amount of nitrogen excreted by cows in the case of NH_3 and N_2O emissions. Emission factors were provided for different manure management systems, but

Table 4
Uncertainty analysis of total NH_3- N, CH_4, $N_2O_{indirect}$ and N_2O_{direct} measured and Tier 3 estimated emissions, using Monte Carlo simulation for total emission value at the biogas plant. Confidence interval: 95%. Included parameters are: Mean, median, SD (Standard Deviation), CV (Coefficient of variation), confidence interval limit 2.5%, confidence interval limit 95.7% and SEM (standard error of the mean).

Emissions		Unit	Mean	Median	SD	CV (%)	2.5%	97.5%	SEM
Emission analysis									
NH_3- N	measurement	kg	2.3E+04	2.1E+04	8.1E+03	35.3	1.1E+04	4.2E+04	80.5
	Tier 3 IPCC	kg	3.3E+04	3.3E+04	2.6E+03	8.1	2.8E+04	3.8E+04	26.4
CH_4	measurement	kg	2.4E+04	6.1E+03	7.8E+04	329.6	2.4E+02	1.5E+05	780.4
	Tier 3 IPCC	kg	1.1E+04	1.0E+04	2.5E+03	23.5	6.5E+03	1.6E+04	25.0
$N_2O_{indirect}$	measurement	kg	3.6E+02	3.4E+02	1.3E+02	35.7	1.7E+02	6.7E+02	1.3
	Tier 3 IPCC	kg	5.0E+02	5.0E+02	4.1E+01	8.1	4.2E+02	5.8E+02	0.4
N_2O_{direct}	measurement	kg	2.6E+02	2.6E+02	5.0E+01	18.9	1.8E+02	3.7E+02	0.5
	Tier 3 IPCC	kg	2.7E+01	2.6E+01	7.7E+00	28.5	1.5E+01	4.5E+01	0.1
H_2S	measurement	kg	8.5E+02	3.5E+02	2.0E+03	239.5	2.5E+01	4.7E+03	20.3
Emission comparison		% measure ≥ estimate							
NH_3- N	measurement - estimate	12.2	−1.0E+04	−1.1E+04	8.4E+03	−84	−2.3E+04	1.0E+04	83.8
CH_4	measurement - estimate	37.8	1.4E+04	−4.1E+03	1.1E+05	774	−1.4E+04	1.5E+05	1075.3
$N_2O_{indirect}$	measurement - estimate	13.7	−1.4E+02	−1.6E+02	1.3E+02	−96	−3.5E+02	1.8E+02	1.3
N_2O_{direct}	measurement - estimate	100.0	2.4E+02	2.3E+02	5.0E+01	21	1.5E+02	3.5E+02	0.5

there were no available factors either for the digestate, for the solid fraction or the liquid fraction, after the solid-liquid separation of digestate. Therefore, it was necessary to establish a hypothesis and, based on the existing literature, select emission factors and additional considerations such as the distribution of N and VS depending on mechanical separation efficiencies and the decrease in VS after anaerobic digestion (see section 2.4.1 to 2.4.3), to estimate the emissions for the scenario under study. All these considerations could be used for further studies.

The selection of emission factors was a critical point. For ammonia emissions, many studies were found providing data for emissions produced by the digestate storage compartment. NH_3 emissions from uncovered digested slurry were twice as those from untreated dairy cattle slurry, due to the high NH_4-N content and the pH value of anaerobically digested slurry (Amon et al., 2006; Clemens et al., 2006; Maurer and Müller, 2012). Few studies were found for cattle emissions of the digestate fractions after liquid-solid separation (Holly et al., 2017; Perazzolo et al., 2015). IPCC NH_3 estimated emission factors were 40% and 30% of the total N content of the slurry in LFS and SFS, respectively. Considering field-measured emissions and TKN amount at the final storage pond, the estimated NH_3 emission factor rose to 28.6%; and to 42.9% when applying TKN balance between the final storage pond and the liquid fraction, which was a little higher than the IPCC NH_3 emission factor (40%). In view of the results of this study and the factors reported in literature, NH_3-N emission factor variability for manure digestate could be observed. Therefore, more biogas plants should be analysed to determine specific emission factors for manure after anaerobic digestion.

On the other hand, annual NH_3-N emissions obtained by field measurements were lower than in any of the IPCC estimates. This low value could be because not all NH_3-N emissions at the plant were measured, since there might be losses at the plant which were not accounted for (such as losses during the mechanical liquid-solid separation of the digestate). The high NH_3-N emissions value obtained with the mass balance method, confirm this hypothesis.

When it comes to CH_4 emissions estimation, a literature review was conducted to search for the maximum methane producing capacities (B_0) of the different digestate fractions, and MCFs for Tier 1 and Tier 2 calculations. B_0 may be influenced by the proportion and type of manure and co-substrate, and the HRT of the reactor (Amon et al., 2006; Gioelli et al., 2011; Lehtomäki et al., 2007; Rico et al., 2011; Thygesen et al., 2014). A B_0 of 0.121 m^3 $CH_4 \cdot kg$ VS^{-1} was reported by Rodhe et al. (2015) in a digestate from the anaerobic co-digestion of cattle manure (95%) and food waste and solid cattle manure (5%). This was the selected value, it being obtained in a similar scenario to the study in case. Nevertheless, CH_4 estimated emissions in Tier 1 and Tier 2 might have been overestimated, as the factor used was obtained from the non-separated digestate storage compartment.

For Tier 3, and in order to more accurately estimate methane emissions, batch tests of the solid and liquid fractions of the digestate were performed (see section 2.3). The methane potential capacities obtained were much lower than the reported results in literature, maybe due to the different feedstock composition, the climate conditions in the area and the long HRT. From field measurement emissions and the VS content of manure, the calculated methane production capacities were 0.214 m^3 $CH_4 \cdot kg$ VS^{-1} for LFS and 0.533 $CH_4 \cdot m^3$ kg VS^{-1} for SFS. These values are much higher than those obtained from the batch tests, indicating a discrepancy in the methane potential VS capacity, from experimental to calculation methods. In view of this variability in results from tests, calculations and literature, more studies to harmonize the methane potential capacity in different types of manure would be convenient.

Total field measurement methane emissions were higher than estimates. For instance, the difference between field-measured total value and Tier 3 total estimate could be explained by the low methane capacity of VS in the digestate samples obtained for the batch tests. Moreover, there arose the possibility that a certain quantity of CH_4 gas could have been retained in the digestate after anaerobic digestion, its later release in storage producing higher emissions. It has been described that up to 20% of biogas could be released in the digestate storage compartment (DEA, 1995). According to the results in this study, it seems that the adapted IPCC models underestimate potential CH_4 emissions. These findings are similar to those reported by Owen and Silver (2015), who compared greenhouse emissions from dairies of thirty-eight studies with Tier 2 modelled values. The study concluded that current greenhouse gas emission factors generally underestimate emissions from dairy manure and that more field data are needed to refine models. It has been found that measurements were higher than Tier 1, Tier 2 and Tier 3 estimates. In Tier 3 estimations, MCFs were selected according to the average annual temperature, being the same for all Tiers. Difference in results were mainly due to the different amount of VS used to estimate emissions. Even though the initial amount of VS was the highest in Tier 3, total yearly emissions were the lowest of the three Tiers. Since most of CH_4 emissions were produced in LFS, a lower VS content in LFS from analytical data used to estimate in Tier 3 provided fewer emissions in Tier 3 than in Tier 1 and Tier 2.

Authors reported that N_2O_{direct} estimated emissions were less than half compared to field-measured emissions in anaerobic lagoons and piles, but greater than in the slurry storage compartment. Contrarily, N_2O_{direct} measurements were 9.4-fold higher than Tier 3 estimates in the present study. This could be explained by the fact that the N_2O_{direct} emission factor at the liquid slurry storage compartment was considered to be zero, according to IPCC guidelines, even if it was found to be present in the samples taken.

As for H_2S emissions, results showed that emission rates were higher in IS (pH 6.4) than in LFS (pH 8.1) and SFS (pH 8.0) (Table 3). These results are in concordance with results from Andriamanohiarisoamanana et al. (2015) and Sutaryo et al. (2012), who concluded that pH has a great influence on sulphide emission rates from dairy manure.

A Monte Carlo analysis was carried out to examine the uncertainties of emissions. This method has been used for the statistical analysis of emissions released in electricity production studies (Fantin et al., 2015; Maurice et al., 2000; Sonnemann et al., 2003), or in emission inventories (Ramírez et al., 2008). CH_4 and H_2S total emissions showed the highest coefficients of variation. On the other hand. The comparison of emission distribution functions delivered that the probability of Tier 3 estimates to be higher than measurements was 88% for NH_3-N, 86% for $N_2O_{indirect}$, 62% for CH_4 and null for N_2O_{direct} total emission values.

A reference situation was defined to distinguish the current manure management practices from the situation previous to the implementation of the biogas treatment plant (see Section 3 of Supplementary information). Comparing the current situation with the reference situation, CH_4, NH_3-N and indirect N_2O total emissions were lower in the current situation, demonstrating the potential benefits of manure processing at a biogas plant (Table S6 in supplementary information). The highest reductions were for CH_4. Comparing total CH_4 measurements in the current situation with Tier 1, Tier 2 and Tier 3 estimates in the reference situation, reductions were 69%, 64% and 80%, respectively.

The characterisation of a biogas plant by field measurements is a complex task and not always possible. The alternative is model estimation according to the specific situation. In this sense, and from the results of this study, emission estimations following the adapted approaches for a biogas plant proposed in this study could be used to determine by-product emissions from anaerobic digestion in similar scenarios. Emission follow-up in this type of manure management system could be useful for decision making, in order to mitigate emissions and contribute with cleaner manure management practices. In this sense, emissions should be estimated with as much precision as possible to attain accurate results. Therefore, further research could focus on determining specific emission factors in different biogas plants to achieve this goal.

5. Conclusions

Emissions at an anaerobic co-digestion plant were characterized by field measurements and IPCC estimation approaches. IPCC guidelines were adapted using emission factors and several considerations for the specific conditions. In Tier 1 and Tier 2, data from literature were used. In Tier 3, analytical data were used. Comparing measurements with estimations, results were found to be in the same order of magnitude. However, more accurate emission factors from field measurements are needed, which might be useful for preparing gaseous emission inventories for waste management systems environmental assessments. On the other hand, biogas plants can be considered an efficient solution to reduce emissions from traditional manure storage, as NH_3-N, CH_4 and $N_2O_{indirect}$ emissions from by-products storage after anaerobic digestion were lower than those from manure stored in an uncovered pond in a reference situation.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2018.01.023.

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